

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-079386  
 (43)Date of publication of application : 24.03.1998

(51)Int.Cl. H01L 21/316  
 H01L 21/31

(21)Application number : 08-253723 (71)Applicant : KOKUSAI ELECTRIC CO LTD  
 (22)Date of filing : 04.09.1996 (72)Inventor : SUZAKI KENICHI

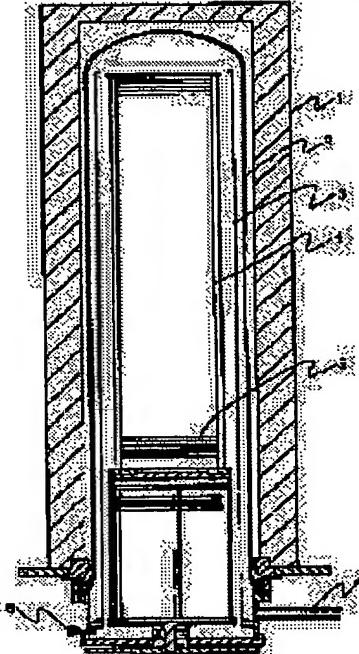
## (54) METHOD OF FORMING SILICON DIOXIDE FILM

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To avoid the production of silicon cluster by a method wherein the silicon dioxide film is chemical-vapor-deposited on a substrate meeting a specific pressure reducing requirements in a mixed growing gas with nitrous oxide containing a specific amount of monosilane.

**SOLUTION:** The lower end of an inner reaction tube 3 is communicated with a gas leading pipe 6 connected to a growing gas supply source so as to supply a growing gas containing SiH<sub>4</sub> and N<sub>2</sub>O to a reaction chamber.

Besides, the lower end of an outer reaction tube 2 is communicated with an exhaust pipe 7 so as to exhaust the gas in the reaction chamber. Accordingly, the growing gas led in from the leading pipe 6 runs in the inner reaction tube 3 containing a wafer 5 so as to produce SiO<sub>2</sub> at a specific heating temperature for the formation of an SiO<sub>2</sub> film on the wafer 5. Through these procedures, the pressure in the reaction chamber is reduced at the state exceeding 40Pa by adjusting the gas supply amount from the gas leading pipe 6 and the exhaust amount from the exhaust pipe 7 so that the ratio of SiH<sub>4</sub> of the growing gas may not exceed 2mol% to the total amount of SiH<sub>4</sub>, and N<sub>2</sub>O.



### LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's  
decision of rejection]

[Date of extinction of right]

**\* NOTICES \***

JPOL and INPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**CLAIMS**

---

**[Claim(s)]**

[Claim 1] The formation approach of the silicon dioxide film characterized by having considered as reduced pressure conditions at least 40Pa or more, and making the rate of the mono silane of said growth gas into 2.0% or less by the mole ratio to the total quantity of a mono silane and nitrous oxide in the approach of making carry out chemical vapor deposition of the silicon dioxide film, and forming it on a substrate in the growth gas containing a mono silane and nitrous oxide.

---

[Translation done.]

**\* NOTICES \***

JP1 and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**DETAILED DESCRIPTION**

---

**[Detailed Description of the Invention]****[0001]**

**[Field of the Invention]** This invention relates to the approach of forming the silicon dioxide film on a substrate with chemical vapor growth (CVD).

**[0002]**

**[Description of the Prior Art]** In the process in which semiconductor devices, such as an MOS mold memory device (MOSRAM) and a static memory component (SRAM), are manufactured, forming gate dielectric film, the passivation film, an interlayer insulation film, etc. with a silicon dioxide (SiO<sub>2</sub>) on substrates, such as a silicon wafer, is performed. Formation of the silicon dioxide film by chemical vapor deposition (CVD method) loads with the wafer which a fission reactor is made to form, and is performed by supplying growth gas to this fission reactor.

**[0003]** A mono silane (SiH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O) are contained in growth gas, and, generally the silicon dioxide film (SiO<sub>2</sub> film) is generated by SiH<sub>4</sub>+2N<sub>2</sub>O=SiO<sub>2</sub>+2H<sub>2</sub>O+4N<sub>2</sub> on a wafer under the generation temperature of about 700 degrees C of a fission reactor thru/or about 850 degrees C. In formation of SiO<sub>2</sub> film by such conventional CVD method, growth gas used what contains SiH<sub>4</sub> 2.5% or more by the mole ratio to the total quantity of SiH<sub>4</sub> and N<sub>2</sub>O.

**[0004]**

**[Problem(s) to be Solved by the Invention]** However, if it was in formation of SiO<sub>2</sub> film by the conventional CVD method, there was a problem that a projection (silicon cluster) with a magnitude of about hundreds of Å will be formed in the front face of SiO<sub>2</sub> generated film. When SiO<sub>2</sub> film with which such a silicon cluster was formed is used as gate dielectric film of for example, a semiconductor memory component, predetermined gate pressure-proofing will not be obtained but the dependability of a component will fall remarkably. For this reason, the wafer with which the silicon cluster has been formed could not be used because of formation of a semiconductor device, but the product yield had fallen remarkably.

**[0005]** This invention was made in view of the above-mentioned conventional situation, and aims at offering the formation approach of the silicon dioxide film which prevented generating of a silicon cluster.

**[0006]**

**[Means for Solving the Problem]** In order to attain the above-mentioned purpose, the formation approach of the silicon dioxide film concerning this invention is characterized by having considered as reduced pressure conditions at least 40Pa or more, and making the rate of the mono silane of said growth gas into 2.0% or less by the mole ratio to the total quantity of a mono silane and nitrous oxide in the approach of making carry out chemical vapor deposition of the silicon dioxide film, and forming it on a substrate, in the growth gas containing a mono silane and nitrous oxide.

**[0007]** In generation of SiO<sub>2</sub> film by the CVD method, a flow and pressure requirement will decline [the growth rate of low voltage past \*\* and SiO<sub>2</sub> film] considerably, and the homogeneity of the thickness distribution of SiO<sub>2</sub> film generated on the other hand when the pressure was too high which is not practical will fall. Moreover, when the mole ratio of SiH<sub>4</sub> contained in growth gas is not much high, a silicon cluster will occur on SiO<sub>2</sub> film generated by

SiH<sub>4</sub> concentration under a reduced pressure condition becoming high beyond the need. so, by the approach of this invention according to claim 1 A practical growth rate is realized by carrying out reduced pressure conditions to more than at least 40Pa (pascal). With this SiH<sub>4</sub> concentration is lowered for the rate of SiH<sub>4</sub> of growth gas as 2% or less by the mole ratio to the total quantity of SiH<sub>4</sub> and N<sub>2</sub>O, the absolute magnitude of SiH<sub>4</sub> molecule in growth gas is controlled, and SiO<sub>2</sub> film is formed, preventing generating of a silicon cluster.

[0008] About generating of the silicon cluster in formation of SiO<sub>2</sub> film by the CVD method, if it will be hard coming to generate a silicon cluster if a flow and pressure requirement serves as high pressure, and SiH<sub>4</sub> concentration becomes small, a silicon cluster will stop being able to tending to generate easily. A certain thing [ that the relation between this flow and pressure requirement and SiH<sub>4</sub> concentration will form SiO<sub>2</sub> film, without generating a silicon cluster if extent correlation is carried out and these both conditions are combined practically ] is possible.

[0009]

[Embodiment of the Invention] The formation approach of the silicon dioxide film concerning this invention is explained based on an example. First, the equipment which enforces the formation approach of the silicon dioxide film concerning this invention is explained with reference to drawing 1. This equipment is equipped with the boat 4 holding the wafer 5 for membrane formation in the tubed heater 1, the external coil 2 held in the interior of a heater 1, the internal coil 3 held in the interior of the external coil 2, and the internal coil 3. The external coil 2 is forming the reaction chamber which upper limit was closed and connoted the internal coil 3, and upper limit is opened wide and it is opening the internal coil 3 for free passage to the reaction chamber concerned. SiO<sub>2</sub> film is formed in the wafer 5 which this reaction chamber was heated at the heater 1, and was held in the reaction chamber under the predetermined temperature of 700 degrees C thru/or 850 degrees C.

[0010] The gas installation tubing 6 is opened for free passage by the lower limit section of the internal coil 3, and the growth gas which the source of growth gas supply outside drawing is connected to the gas installation tubing 6, and contains SiH<sub>4</sub> and N<sub>2</sub>O in a reaction chamber is supplied. Moreover, the exhaust pipe 7 connected to the exhauster outside drawing is opened for free passage by the lower limit section of the external coil 2, and the gas in a reaction chamber is exhausted from an exhaust pipe 7. Therefore, the growth gas introduced from the gas installation tubing 6 flows the inside of the internal coil 3 which held the wafer 5, generates SiO<sub>2</sub> whenever [ predetermined stoving temperature ] in the bottom, and makes SiO<sub>2</sub> film form on a wafer 5. The pressure in a reaction chamber has come change into a reduced pressure condition 40Pa or more here by adjustment with the gas supply volume from the gas installation tubing 6, and the displacement from an exhaust pipe 7.

[0011] Moreover, at the membrane formation process of SiO<sub>2</sub> film in SiH<sub>4</sub> and N<sub>2</sub>O, generally, it is carried out in 700 degrees C – 850 degrees C, a temperature gradient is set up in said temperature requirement towards the upper part from the lower part of a heater 1, and the direction of the lower part of a heater 1 is set as temperature lower than the upper part. Thus, since reactant gas is exhausted and gas concentration becomes low as reactant gas concentration is high and goes up like the lower part of a heater 1, i.e., the reaction chamber bottom, the reason for establishing a temperature gradient is for making thickness in the lower part equivalent from the upper part according to a temperature gradient.

[0012] The pressure in a reaction chamber was made into three kinds, 40Pa, 80Pa, and 160Pa, and SiO<sub>2</sub> film with a thickness of 300A was formed [ the rate of SiH<sub>4</sub> contained in growth gas ] for the mole ratio and the quantity of gas flow all over the principal plane of the silicon wafer 5 with a diameter of 8 inches as the five following kinds to the total quantity of SiH<sub>4</sub> and N<sub>2</sub>O in above equipment. SiH<sub>4</sub> by (1) mole ratio by 1/30 (namely, about 3.4%) and the quantity of gas flow Namely, 35SCCM(s), N<sub>2</sub>O by 1050SCCM(s) and (2) mole ratios 1/40 (namely, 2.5%), For SiH<sub>4</sub>, 27SCCM(s) and N<sub>2</sub>O is 1/50 () at 1050SCCM(s) and (3) mole ratios in a quantity of gas flow. 21SCCM(s) and N<sub>2</sub>O by the quantity of gas flow 2.0% Namely, 1050SCCM(s), [ SiH<sub>4</sub> ] (4) — a mole ratio — 1/60 (namely, about 1.7%) and a quantity of gas flow — SiH<sub>4</sub> — by the quantity of gas flow, 15SCCM(s) and N<sub>2</sub>O was as 1/70 (namely, about 1.4%) by 1050SCCM(s) and (5) mole

ratios, and SiH<sub>4</sub> could be [ 18SCCM(s) and N<sub>2</sub>O ] five kinds of 1050SCCM(s). The result to which the scale factor 60,000 carried out SEM observation of the SiO<sub>2</sub> film formed of this experiment is shown in Table 1 thru/or 3, respectively.

[0013]

[Table 1]

圧力 40Pa

SiH <sub>4</sub> モル比	シリコンクラスタ の有無	屈折率	成膜速度 Å/min	膜厚均一性 ±%
1 / 30	○	1.29	17.6	9.0 以下
1 / 40	○	0.98	14.8	2.8 以下
1 / 50	×	0.78	12.4	2.5 以下
1 / 60	×	0.66	11.0	2.5 以下
1 / 70	×	0.58	10.5	2.5 以下

[0014]

[Table 2]

圧力 80Pa

SiH <sub>4</sub> モル比	シリコンクラスタ の有無	屈折率	成膜速度 Å/min	膜厚均一性 ±%
1 / 30	○	2.58	31.0	5.0 以下
1 / 40	×	1.95	23.8	3.0 以下
1 / 50	×	1.57	20.2	3.0 以下
1 / 60	×	1.31	18.0	2.8 以下
1 / 70	×	1.13	16.1	2.6 以下

[0015]

[Table 3]

圧力 160Pa

SiH <sub>4</sub> モル比	シリコンクラスタ の有無	屈折率	成膜速度 Å/min	膜厚均一性 ±%
1 / 30	×	5.16	55.2	7.5 以下
1 / 40	×	3.90	45.0	7.0 以下
1 / 50	×	3.14	36.8	6.0 以下
1 / 60	×	2.62	31.4	5.5 以下
1 / 70	×	2.26	27.4	4.0 以下

[0016] The observation result about SiO<sub>2</sub> film which was formed in the pressure of 40Pa and Table 2 by the pressure of 80Pa, and was formed in Table 3 by 160Pa is shown in Table 1, and it is made to correspond to the mole ratio of SiH<sub>4</sub> contained in growth gas in each table, and X mark is described, when existence of a silicon cluster is observed and O mark and existence of a silicon cluster are not observed. In addition, thickness homogeneity measures the thickness of two or more points in the circumferencial direction in a wafer, and the direction of circles of longitude at equal intervals, and takes out deflection to them. Moreover, a membrane formation rate is broken by deposition time amount to the average thickness of a lower wafer into a top in a wafer processing field. Moreover, according to the refractive index, the crystallized state (membraneous quality) of membrane formation can be judged.

[0017] If a flow and pressure requirement serves as high pressure from the above-mentioned table about generating of the silicon cluster in SiO<sub>2</sub> formed film, it will be hard coming to

generate a silicon cluster, and if the mole ratio of SiH<sub>4</sub> becomes small, it turns out that a silicon cluster stops being able to tending to generate easily. Thus, by generation of SiO<sub>2</sub> film by the CVD method, if a pressure is high, the passing speed of SiH<sub>4</sub> molecule in growth gas and an N<sub>2</sub>O molecule can loosen, decomposition of N<sub>2</sub>O is performed smoothly, and the reason which a silicon cluster will stop being able to generate easily if a flow and pressure requirement serves as high pressure is considered that generating of a silicon cluster is controlled by this. Moreover, the reason which a silicon cluster will stop being able to generate easily if the mole ratio of SiH<sub>4</sub> becomes small is considered for the probability for Si atom to serve as the aggregate to fall, when SiH<sub>4</sub> concentration in growth gas falls and the absolute magnitude of SiH<sub>4</sub> molecule decreases.

[0018] And generating of the silicon cluster in 1/50 or less [ then ] and SiO<sub>2</sub> film does not have reduced pressure conditions in the mole ratio of SiH<sub>4</sub> at 40Pa so that clearly from the above-mentioned table. Generating of the silicon cluster in 1/40 or less [ then ] and SiO<sub>2</sub> film did not have reduced pressure conditions in the mole ratio of SiH<sub>4</sub> at 80Pa, and generating of the silicon cluster in SiO<sub>2</sub> film did not have reduced pressure conditions considering the mole ratio of SiH<sub>4</sub> as 1/30 at 160Pa. Therefore, it is possible by setting reduced pressure conditions to 40Pa thru/or 160Pa, and combining these both conditions for the rate of SiH<sub>4</sub> of growth gas as below 1/50 (namely, 2.0%) by the mole ratio to the total quantity of SiH<sub>4</sub> and N<sub>2</sub>O to form SiO<sub>2</sub> film, without generating a silicon cluster practically.

[0019] If it says from a practical use side, while a membrane formation rate becomes slow, membrane formation time amount will require for 40Pa or less seriously and the amount of the expensive reactant gas used will increase, a serious fault causes the fall of a throughput, as a result delay of a back process by the throughput fall of equipment, and is not suitable for the production process of a semiconductor device. Therefore, it is good to be 2.0 or less-mole ratio conditions, and to choose a pressure and a mole ratio suitably by 40Pa or more, in consideration of practical membrane formation rate thickness homogeneity and not producing a big change of a refractive index, as further shown in drawing 2.

[0020]

[Effect of the Invention] As explained above, according to the formation approach of the silicon dioxide concerning this invention, by setting up reduced pressure conditions and the mono-silane concentration in growth gas, generating of a silicon cluster can be prevented and the silicon dioxide film can be formed. And reduced pressure conditions are set to at least 40Pa or more, the rate of the mono silane in growth gas is written as 2.0% or less by the mole ratio to the total quantity of a mono silane and nitrous oxide, and the silicon dioxide film with the very high homogeneity of film pressure distribution can be formed with a practical growth rate, without generating a silicon cluster. Therefore, since generating of the silicon cluster in the formed silicon dioxide film can be prevented according to the formation approach of the silicon dioxide concerning this invention as a result, the effectiveness that the semiconductor device excellent in engine performance, such as withstand voltage, can be manufactured also does so.

---

[Translation done.]

**\* NOTICES \***

JP@ and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**TECHNICAL FIELD**

---

[Field of the Invention] This invention relates to the approach of forming the silicon dioxide film on a substrate with chemical vapor growth (CVD).

---

[Translation done.]

**\* NOTICES \***

JPO and INPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**PRIOR ART**

---

[Description of the Prior Art] In the process in which semiconductor devices, such as an MOS mold memory device (MOSRAM) and a static memory component (SRAM), are manufactured, forming gate dielectric film, the passivation film, an interlayer insulation film, etc. with a silicon dioxide (SiO<sub>2</sub>) on substrates, such as a silicon wafer, is performed. Formation of the silicon dioxide film by chemical vapor deposition (CVD method) loads with the wafer which a fission reactor is made to form, and is performed by supplying growth gas to this fission reactor.

[0003] A mono silane (SiH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O) are contained in growth gas, and, generally the silicon dioxide film (SiO<sub>2</sub> film) is generated by SiH<sub>4</sub>+2N<sub>2</sub>O=SiO<sub>2</sub>+2H<sub>2</sub>O+4N<sub>2</sub> on a wafer under the generation temperature of about 700 degrees C of a fission reactor thru/or about 850 degrees C. In formation of SiO<sub>2</sub> film by such conventional CVD method, growth gas used what contains SiH<sub>4</sub> 2.5% or more by the mole ratio to the total quantity of SiH<sub>4</sub> and N<sub>2</sub>O.

---

[Translation done.]

**\* NOTICES \***

JPO and INPI are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

**EFFECT OF THE INVENTION**

---

[Effect of the Invention] As explained above, according to the formation approach of the silicon dioxide concerning this invention, by setting up reduced pressure conditions and the mono-silane concentration in growth gas, generating of a silicon cluster can be prevented and the silicon dioxide film can be formed. And reduced pressure conditions are set to at least 40Pa or more, the rate of the mono silane in growth gas is written as 2.0% or less by the mole ratio to the total quantity of a mono silane and nitrous oxide, and the silicon dioxide film with the very high homogeneity of film pressure distribution can be formed with a practical growth rate, without generating a silicon cluster. Therefore, since generating of the silicon cluster in the formed silicon dioxide film can be prevented according to the formation approach of the silicon dioxide concerning this invention as a result, the effectiveness that the semiconductor device excellent in engine performance, such as withstand voltage, can be manufactured also does so.

---

[Translation done.]

**\* NOTICES \***

JPPO and INPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**TECHNICAL PROBLEM**

---

[Problem(s) to be Solved by the Invention] However, if it was in formation of SiO<sub>2</sub> film by the conventional CVD method, there was a problem that a projection (silicon cluster) with a magnitude of about hundreds of Å will be formed in the front face of SiO<sub>2</sub> generated film. When SiO<sub>2</sub> film with which such a silicon cluster was formed is used as gate dielectric film of for example, a semiconductor memory component, predetermined gate pressure-proofing will not be obtained but the dependability of a component will fall remarkably. For this reason, the wafer with which the silicon cluster has been formed could not be used because of formation of a semiconductor device, but the product yield had fallen remarkably.

[0005] This invention was made in view of the above-mentioned conventional situation, and aims at offering the formation approach of the silicon dioxide film which prevented generating of a silicon cluster.

---

[Translation done.]

**\* NOTICES \***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

**MEANS**

---

[Means for Solving the Problem] In order to attain the above-mentioned purpose, the formation approach of the silicon dioxide film concerning this invention is characterized by having considered as reduced pressure conditions at least 40Pa or more, and making the rate of the mono silane of said growth gas into 2.0% or less by the mole ratio to the total quantity of a mono silane and nitrous oxide in the approach of making carry out chemical vapor deposition of the silicon dioxide film, and forming it on a substrate, in the growth gas containing a mono silane and nitrous oxide.

[0007] In generation of SiO<sub>2</sub> film by the CVD method, a flow and pressure requirement will decline [ the growth rate of low voltage past \*\* and SiO<sub>2</sub> film ] considerably, and the homogeneity of the thickness distribution of SiO<sub>2</sub> film generated on the other hand when the pressure was too high which is not practical will fall. Moreover, when the mole ratio of SiH<sub>4</sub> contained in growth gas is not much high, a silicon cluster will occur on SiO<sub>2</sub> film generated by SiH<sub>4</sub> concentration under a reduced pressure condition becoming high beyond the need. so, by the approach of this invention according to claim 1 A practical growth rate is realized by carrying out reduced pressure conditions to more than at least 40Pa (pascal). With this SiH<sub>4</sub> concentration is lowered for the rate of SiH<sub>4</sub> of growth gas as 2% or less by the mole ratio to the total quantity of SiH<sub>4</sub> and N<sub>2</sub>O, the absolute magnitude of SiH<sub>4</sub> molecule in growth gas is controlled, and SiO<sub>2</sub> film is formed, preventing generating of a silicon cluster.

[0008] About generating of the silicon cluster in formation of SiO<sub>2</sub> film by the CVD method, if it will be hard coming to generate a silicon cluster if a flow and pressure requirement serves as high pressure, and SiH<sub>4</sub> concentration becomes small, a silicon cluster will stop being able to tending to generate easily. A certain thing [ that the relation between this flow and pressure requirement and SiH<sub>4</sub> concentration will form SiO<sub>2</sub> film, without generating a silicon cluster if extent correlation is carried out and these both conditions are combined practically ] is possible.

**[0009]**

[Embodiment of the Invention] The formation approach of the silicon dioxide film concerning this invention is explained based on an example. First, the equipment which enforces the formation approach of the silicon dioxide film concerning this invention is explained with reference to drawing 1 . This equipment is equipped with the boat 4 holding the wafer 5 for membrane formation in the tubed heater 1, the external coil 2 held in the interior of a heater 1, the internal coil 3 held in the interior of the external coil 2, and the internal coil 3. The external coil 2 is forming the reaction chamber which upper limit was closed and connoted the internal coil 3, and upper limit is opened wide and it is opening the internal coil 3 for free passage to the reaction chamber concerned. SiO<sub>2</sub> film is formed in the wafer 5 which this reaction chamber was heated at the heater 1, and was held in the reaction chamber under the predetermined temperature of 700 degrees C thru/or 850 degrees C.

[0010] The gas installation tubing 6 is opened for free passage by the lower limit section of the internal coil 3, and the growth gas which the source of growth gas supply outside drawing is connected to the gas installation tubing 6, and contains SiH<sub>4</sub> and N<sub>2</sub>O in a reaction chamber is supplied. Moreover, the exhaust pipe 7 connected to the exhauster outside drawing is opened for

free passage by the lower limit section of the external coil 2, and the gas in a reaction chamber is exhausted from an exhaust pipe 7. Therefore, the growth gas introduced from the gas installation tubing 6 flows the inside of the internal coil 3 which held the wafer 5, generates SiO<sub>2</sub> whenever [ predetermined stoving temperature ] in the bottom, and makes SiO<sub>2</sub> film form on a wafer 5. The pressure in a reaction chamber has come change into a reduced pressure condition 40Pa or more here by adjustment with the gas supply volume from the gas installation tubing 6, and the displacement from an exhaust pipe 7.

[0011] Moreover, at the membrane formation process of SiO<sub>2</sub> film in SiH<sub>4</sub> and N<sub>2</sub>O, generally, it is carried out in 700 degrees C – 850 degrees C, a temperature gradient is set up in said temperature requirement towards the upper part from the lower part of a heater 1, and the direction of the lower part of a heater 1 is set as temperature lower than the upper part. Thus, since reactant gas is exhausted and gas concentration becomes low as reactant gas concentration is high and goes up like the lower part of a heater 1, i.e., the reaction chamber bottom, the reason for establishing a temperature gradient is for making thickness in the lower part equivalent from the upper part according to a temperature gradient.

[0012] The pressure in a reaction chamber was made into three kinds, 40Pa, 80Pa, and 160Pa, and SiO<sub>2</sub> film with a thickness of 300A was formed [ the rate of SiH<sub>4</sub> contained in growth gas ] for the mole ratio and the quantity of gas flow all over the principal plane of the silicon wafer 5 with a diameter of 8 inches as the five following kinds to the total quantity of SiH<sub>4</sub> and N<sub>2</sub>O in above equipment SiH<sub>4</sub> by (1) mole ratio by 1/30 (namely, about 3.4%) and the quantity of gas flow Namely, 35SCCM(s), N<sub>2</sub>O by 1050SCCM(s) and (2) mole ratios 1/40 (namely, 2.5%), For SiH<sub>4</sub>, 27SCCM(s) and N<sub>2</sub>O is 1/50 () at 1050SCCM(s) and (3) mole ratios in a quantity of gas flow. 21SCCM(s) and N<sub>2</sub>O by the quantity of gas flow 2.0% Namely, 1050SCCM(s), [ SiH<sub>4</sub> ] (4) — a mole ratio — 1/60 (namely, about 1.7%) and a quantity of gas flow — SiH<sub>4</sub> — by the quantity of gas flow, 15SCCM(s) and N<sub>2</sub>O was as 1/70 (namely, about 1.4%) by 1050SCCM(s) and (5) mole ratios, and SiH<sub>4</sub> could be [ 18SCCM(s) and N<sub>2</sub>O ] five kinds of 1050SCCM(s). The result to which the scale factor 60,000 carried out SEM observation of the SiO<sub>2</sub> film formed of this experiment is shown in Table 1 thru/or 3, respectively.

[0013]

[Table 1]

圧力 40Pa

SiH <sub>4</sub> モル比	シリコンクラスタ の有無	屈折率	成膜速度 Å/min	膜厚均一性 ±%
1 / 30	○	1.29	17.6	3.0 以下
1 / 40	○	0.98	14.8	2.8 以下
1 / 50	×	0.78	12.4	2.5 以下
1 / 60	×	0.66	11.0	2.5 以下
1 / 70	×	0.56	10.5	2.5 以下

[0014]

[Table 2]

圧力 80Pa

SiH <sub>4</sub> モル比	シリコンクラスタ の有無	屈折率	成膜速度 Å/min	膜厚均一性 ±%
1 / 30	○	2.58	31.0	5.0 以下
1 / 40	×	1.95	23.8	3.0 以下
1 / 50	×	1.57	20.2	3.0 以下
1 / 60	×	1.31	18.0	2.8 以下
1 / 70	×	1.13	16.1	2.6 以下

[0015]

[Table 3]

圧力 160Pa

SiH <sub>4</sub> モル比	シリコンクラスタ の有無	屈折率	成膜速度 Å/min	膜厚均一性 ±%
1 / 80	×	5.16	55.2	7.5以下
1 / 40	×	3.90	45.0	7.0以下
1 / 50	×	3.14	36.8	6.0以下
1 / 60	×	2.82	31.4	5.5以下
1 / 70	×	2.26	27.4	4.0以下

[0016] The observation result about SiO<sub>2</sub> film which was formed in the pressure of 40Pa and Table 2 by the pressure of 80Pa, and was formed in Table 3 by 160Pa is shown in Table 1, and it is made to correspond to the mole ratio of SiH<sub>4</sub> contained in growth gas in each table, and X mark is described, when existence of a silicon cluster is observed and O mark and existence of a silicon cluster are not observed. In addition, thickness homogeneity measures the thickness of two or more points in the circumferential direction in a wafer, and the direction of circles of longitude at equal intervals, and takes out deflection to them. Moreover, a membrane formation rate is broken by deposition time amount to the average thickness of a lower wafer into a top in a wafer processing field. Moreover, according to the refractive index, the crystallized state (membraneous quality) of membrane formation can be judged.

[0017] If a flow and pressure requirement serves as high pressure from the above-mentioned table about generating of the silicon cluster in SiO<sub>2</sub> formed film, it will be hard coming to generate a silicon cluster, and if the mole ratio of SiH<sub>4</sub> becomes small, it turns out that a silicon cluster stops being able to tending to generate easily. Thus, by generation of SiO<sub>2</sub> film by the CVD method, if a pressure is high, the passing speed of SiH<sub>4</sub> molecule in growth gas and an N<sub>2</sub>O molecule can loosen, decomposition of N<sub>2</sub>O is performed smoothly, and the reason which a silicon cluster will stop being able to generate easily if a flow and pressure requirement serves as high pressure is considered that generating of a silicon cluster is controlled by this. Moreover, the reason which a silicon cluster will stop being able to generate easily if the mole ratio of SiH<sub>4</sub> becomes small is considered for the probability for Si atom to serve as the aggregate to fall, when SiH<sub>4</sub> concentration in growth gas falls and the absolute magnitude of SiH<sub>4</sub> molecule decreases.

[0018] And generating of the silicon cluster in 1/50 or less [ then ] and SiO<sub>2</sub> film does not have reduced pressure conditions in the mole ratio of SiH<sub>4</sub> at 40Pa so that clearly from the above-mentioned table. Generating of the silicon cluster in 1/40 or less [ then ] and SiO<sub>2</sub> film did not have reduced pressure conditions in the mole ratio of SiH<sub>4</sub> at 80Pa, and generating of the silicon cluster in SiO<sub>2</sub> film did not have reduced pressure conditions considering the mole ratio of SiH<sub>4</sub> as 1/30 at 160Pa. Therefore, it is possible by setting reduced pressure conditions to 40Pa thru/or 160Pa, and combining these both conditions for the rate of SiH<sub>4</sub> of growth gas as below 1/50 (namely, 2.0%) by the mole ratio to the total quantity of SiH<sub>4</sub> and N<sub>2</sub>O to form SiO<sub>2</sub> film, without generating a silicon cluster practically.

[0019] If it says from a practical use side, while a membrane formation rate becomes slow, membrane formation time amount will require for 40Pa or less seriously and the amount of the expensive reactant gas used will increase, a serious fault causes the fall of a throughput, as a result delay of a back process by the throughput fall of equipment, and is not suitable for the production process of a semiconductor device. Therefore, it is good to be 2.0 or less-mole ratio conditions, and to choose a pressure and a mole ratio suitably by 40Pa or more, in consideration of practical membrane formation rate thickness homogeneity and not producing a big change of a refractive index, as further shown in drawing 2.

[Translation done.]

**\* NOTICES \***

JPO and INPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**DESCRIPTION OF DRAWINGS**

---

**[Brief Description of the Drawings]**

[Drawing 1] It is the sectional view showing an example of the equipment for enforcing the approach concerning this invention.

[Drawing 2] It is the graph which shows the relation between mono-silane concentration and the membranous quality of the silicon dioxide film.

**[Description of Notations]**

- 1 Heater
- 2 External Coil
- 3 Internal Coil
- 4 Boat
- 5 Wafer
- 6 Gas Installation Tubing
- 7 Exhaust Pipe

---

**[Translation done.]**

**\* NOTICES \***

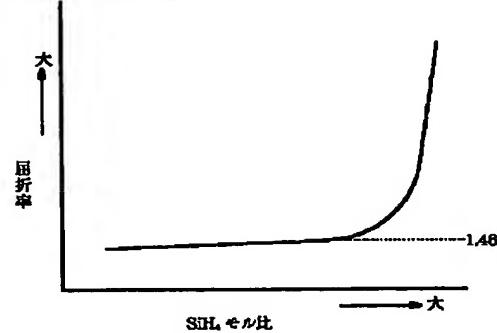
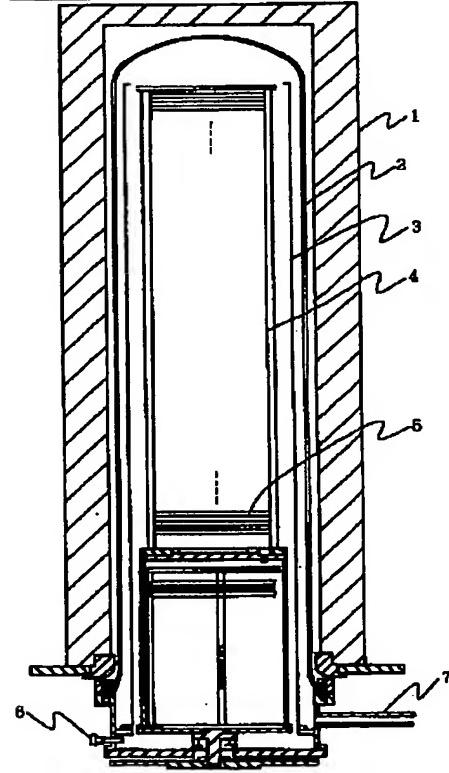
JPO and INPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**DRAWINGS**

---

**[Drawing 2]****[Drawing 1]**

---

[Translation done.]

---

(19)日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11)特許出願公開番号

特開平10-79386

(43)公開日 平成10年(1998)3月24日

(51)Int.Cl.<sup>6</sup>  
H 0 1 L 21/316  
21/31

識別記号  
H 0 1 L 21/316  
21/31

府内整理番号

F I  
H 0 1 L 21/316  
21/31

技術表示箇所  
X  
B

審査請求 未請求 請求項の数1 FD (全 5 頁)

(21)出願番号 特願平8-253723

(22)出願日 平成8年(1996)9月4日

(71)出願人 000001122

国際電気株式会社  
東京都中野区東中野三丁目14番20号

(72)発明者 寿崎 健一

東京都中野区東中野三丁目14番20号 国際  
電気株式会社内

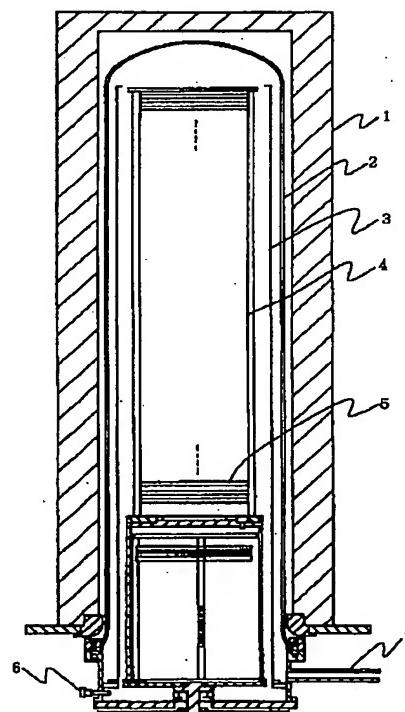
(74)代理人 弁理士 守山 辰雄

(54)【発明の名称】 二酸化珪素膜の形成方法

(57)【要約】

【課題】 シリコンクラスタの発生を防止して二酸化珪素膜を形成する。

【解決手段】 少なくとも40Pa以上の減圧条件とし、成長ガスのモノシランの割合をモノシランと亜酸化窒素との合計量に対してモル比で2.0%以下として、基板5上に二酸化珪素膜を化学気相成長させて形成する。これにより、実用的な成長速度を維持しつつ均一な膜圧分布を実現し、かつ、シリコンクラスタの発生を防止して二酸化珪素膜を形成する。



## 【特許請求の範囲】

【請求項1】 モノシリランと亜酸化窒素とを含む成長ガス中で基板上に二酸化珪素膜を化学気相成長させて形成する方法において、少なくとも40Pa以上の減圧条件とし、前記成長ガスのモノシリランの割合をモノシリランと亜酸化窒素との合計量に対してモル比で2.0%以下としたことを特徴とする二酸化珪素膜の形成方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は化学的気相成長(CVD)により基板上に二酸化珪素膜を形成する方法に関する。

## 【0002】

【従来の技術】 MOS型メモリ素子(MOSRAM)やスタティックメモリ素子(SRAM)等の半導体装置を製造する過程において、シリコンウエーハ等の基板上に二酸化珪素(SiO<sub>2</sub>)でゲート絶縁膜、パッシベーション膜、層間絶縁膜等を形成することが行われている。化学的気相成長法(CVD法)による二酸化珪素膜の形成は、反応炉に成膜させるウエーハを装填し、この反応炉に成長ガスを供給して行われる。

【0003】 成長ガスにはモノシリラン(SiH<sub>4</sub>)と亜酸化窒素(N<sub>2</sub>O)とが含まれており、一般的には反応炉内の約700°C乃至約850°Cの生成温度下で、SiH<sub>4</sub>+2N<sub>2</sub>O=SiO<sub>2</sub>+2H<sub>2</sub>O+4N<sub>2</sub>により、ウエーハ上に二酸化珪素膜(SiO<sub>2</sub>膜)が生成される。このような従来のCVD法によるSiO<sub>2</sub>膜の形成においては、成長ガスはSiH<sub>4</sub>とN<sub>2</sub>Oとの合計量に対してSiH<sub>4</sub>をモル比で2.5%以上含有するものを用いていた。

## 【0004】

【発明が解決しようとする課題】 しかしながら、従来のCVD法によるSiO<sub>2</sub>膜の形成にあっては、生成されたSiO<sub>2</sub>膜の表面に数百オングストローム程度の大きさの突起(シリコンクラスター)が形成されてしまうという問題があった。このようなシリコンクラスターが形成されたSiO<sub>2</sub>膜を、例えば半導体メモリ素子のゲート絶縁膜として用いた場合には、所定のゲート耐圧が得られず、素子の信頼性が著しく低下してしまう。このため、シリコンクラスターが形成されてしまったウエーハは半導体素子の形成のために使用することができず、製品歩留まりが著しく低下してしまっていた。

【0005】 本発明は上記従来の事情に鑑みなされたもので、シリコンクラスターの発生を防止した二酸化珪素膜の形成方法を提供することを目的とする。

## 【0006】

【課題を解決するための手段】 上記目的を達成するため、本発明に係る二酸化珪素膜の形成方法は、モノシリランと亜酸化窒素とを含む成長ガス中で基板上に二酸化珪素膜を化学気相成長させて形成する方法において、少な

くとも40Pa以上の減圧条件とし、前記成長ガスのモノシリランの割合をモノシリランと亜酸化窒素との合計量に対してモル比で2.0%以下としたことを特徴とする。

【0007】 CVD法によるSiO<sub>2</sub>膜の生成では、圧力条件が低圧すぎるとSiO<sub>2</sub>膜の成長速度がかなり低下して実用的でない、一方、圧力が高すぎると生成されたSiO<sub>2</sub>膜の膜厚分布の均一性が低下してしまう。また、成長ガスに含まれるSiH<sub>4</sub>のモル比があまり高い場合には、減圧状態下でのSiH<sub>4</sub>濃度が必要以上に高くなつて生成されたSiO<sub>2</sub>膜にシリコンクラスターが発生してしまう。そこで、請求項1に記載の本発明の方法では、減圧条件を少なくとも40Pa(パスカル)以上として、実用的な成長速度を実現し、これとともに、成長ガスのSiH<sub>4</sub>の割合をSiH<sub>4</sub>とN<sub>2</sub>Oとの合計量に対してモル比で2%以下として、SiH<sub>4</sub>濃度を下げて成長ガス中のSiH<sub>4</sub>分子の絶対量を抑制し、シリコンクラスターの発生を防止しつつSiO<sub>2</sub>膜を形成する。

【0008】 CVD法によるSiO<sub>2</sub>膜の形成におけるシリコンクラスターの発生に関して、圧力条件は高圧となればシリコンクラスターは発生し難くなり、SiH<sub>4</sub>濃度が小さくなればシリコンクラスターは発生し難くなる傾向がある。この圧力条件とSiH<sub>4</sub>濃度との関係は或る程度相関しており、実用上はこれら両者の条件を組み合わせると、シリコンクラスターを発生させることなくSiO<sub>2</sub>膜を形成することが可能である。

## 【0009】

【発明の実施の形態】 本発明に係る二酸化珪素膜の形成方法を実施例に基づいて説明する。まず、本発明に係る二酸化珪素膜の形成方法を実施する装置を図1を参照して説明する。この装置は、筒状のヒータ1と、ヒータ1の内部に収容された外部反応管2と、外部反応管2の内部に収容された内部反応管3と、内部反応管3内に成膜対象のウエーハ5を保持するポート4とを備えている。外部反応管2は上端が閉じられて内部反応管3を内包した反応室を画成しており、内部反応管3は上端が開放されて当該反応室に連通している。この反応室はヒータ1によって加熱されるようになっており、反応室に収容されたウエーハ5には700°C乃至850°Cの所定温度下でSiO<sub>2</sub>膜が形成される。

【0010】 内部反応管3の下端部にはガス導入管6が連通されており、ガス導入管6には図外の成長ガス供給源が接続されて反応室内にSiH<sub>4</sub>とN<sub>2</sub>Oとを含有する成長ガスを供給するようになっている。また、外部反応管2の下端部には図外の排気装置に接続された排気管7が連通されており、排気管7から反応室内のガスを排気するようになっている。したがって、ガス導入管6から導入された成長ガスはウエーハ5を収容した内部反応管3内を流れ、所定の加熱温度下でSiO<sub>2</sub>を生成してウエーハ5上にSiO<sub>2</sub>膜を成膜させる。ここに、ガス導入管6からのガス供給量と排気管7からの排気量との調

整により、反応室内の圧力は40Pa以上の中圧状態にできるようになっている。

【0011】また、SiH<sub>4</sub>とN<sub>2</sub>OでのSiO<sub>2</sub>膜の成膜工程では、一般的に、700℃～850℃の範囲で行われ、ヒータ1の下部から上部に向けて前記温度範囲内で温度勾配が設定され、ヒータ1の下部の方が上部よりも低い温度に設定される。このように温度勾配を設ける理由は、ヒータ1の下部、即ち反応室の下側程、反応ガス濃度が高く、上方に行くに従って反応ガスが消耗されてガス濃度が低くなることから、温度勾配によって上部から下部での膜厚を同等にするためである。

【0012】上記の装置において、反応室内の圧力を40Pa、80Pa、160Paの3通りとし、成長ガス中に含まれるSiH<sub>4</sub>の割合をSiH<sub>4</sub>とN<sub>2</sub>Oとの合計量に対してモル比及びガス流量を下記の5通りとして、直径8インチのシリコンウェーハ5の正面全面に厚さ3\*圧力40Pa

SiH <sub>4</sub> モル比	シリコンクラスタ の有無	屈折率	成膜速度 Å/min	膜厚均一性 ±%
1 / 30	○	1.29	17.8	3.0以下
1 / 40	○	0.98	14.8	2.8以下
1 / 50	×	0.78	12.4	2.5以下
1 / 60	×	0.66	11.0	2.5以下
1 / 70	×	0.58	10.5	2.5以下

【0014】

※※【表2】

SiH <sub>4</sub> モル比	シリコンクラスタ の有無	屈折率	成膜速度 Å/min	膜厚均一性 ±%
1 / 30	○	2.58	31.0	5.0以下
1 / 40	×	1.95	23.8	3.0以下
1 / 50	×	1.57	20.2	3.0以下
1 / 60	×	1.31	18.0	2.8以下
1 / 70	×	1.13	16.1	2.6以下

【0015】

★★【表3】

SiH <sub>4</sub> モル比	シリコンクラスタ の有無	屈折率	成膜速度 Å/min	膜厚均一性 ±%
1 / 30	×	5.16	55.2	7.5以下
1 / 40	×	3.90	45.0	7.0以下
1 / 50	×	3.14	36.8	6.0以下
1 / 60	×	2.62	31.4	5.5以下
1 / 70	×	2.26	27.4	4.0以下

【0016】表1には圧力40Pa、表2には圧力80Pa、表3には160Paで形成されたSiO<sub>2</sub>膜につ

いての観察結果を示してあり、それぞれの表には成長ガス中に含まれるSiH<sub>4</sub>のモル比に対応させて、シリコ

ンクラスタの存在が観察された場合には○印、シリコンクラスタの存在が観察されなかった場合にはX印を記してある。なお、膜厚均一性は、ウエーハ内の円周方向、経線方向に等間隔に複数点の膜厚を測定し、偏差を出したものである。また、成膜速度は、ウエーハ処理領域において、上、中、下部のウエーハの平均膜厚に対してデポジション時間で割ったものである。また、屈折率によれば、成膜の結晶状態（膜質）を判断することができる。

【0017】上記の表から、形成されたSiO<sub>2</sub>膜におけるシリコンクラスタの発生に関して、圧力条件が高圧となればシリコンクラスタは発生し難くなり、SiH<sub>4</sub>のモル比が小さくなればシリコンクラスタは発生し難くなる傾向があることが判る。このように圧力条件が高圧となればシリコンクラスタが発生し難くなる理由は、CVD法によるSiO<sub>2</sub>膜の生成では、圧力が高いと成長ガス中のSiH<sub>4</sub>分子とN<sub>2</sub>O分子との移動速度が緩められて、N<sub>2</sub>Oの分解が円滑に行われ、これによって、シリコンクラスタの発生が抑制されると考えられる。また、SiH<sub>4</sub>のモル比が小さくなればシリコンクラスタが発生し難くなる理由は、成長ガス中のSiH<sub>4</sub>濃度が低下してSiH<sub>4</sub>分子の絶対量が少なくなることにより、Si原子が集合体となる確率が下がるためと考えられる。

【0018】そして、上記の表から明らかのように、減圧条件が40PaではSiH<sub>4</sub>のモル比を1/50以下とすればSiO<sub>2</sub>膜でのシリコンクラスタの発生はなく、減圧条件が80PaではSiH<sub>4</sub>のモル比を1/40以下とすればSiO<sub>2</sub>膜でのシリコンクラスタの発生はなく、減圧条件が160PaではSiH<sub>4</sub>のモル比を1/30としてもSiO<sub>2</sub>膜でのシリコンクラスタの発生はなかった。したがって、減圧条件を40Pa乃至160Paとし、成長ガスのSiH<sub>4</sub>の割合をSiH<sub>4</sub>とN<sub>2</sub>Oとの合計量に対してモル比で1/50（すなわち、2.0%）以下として、これら両者の条件を組み合わせることにより、実用上はシリコンクラスタを発生させることなくSiO<sub>2</sub>膜を形成することが可能である。\*

(4)  
6

\* 【0019】実用面から言えば、40Pa以下では成膜速度が遅くなり、成膜時間が多大に要することになり、高価な反応ガスの使用量が増えると共に、重大な欠点は装置の処理能力低下によりスループットの低下、ひいては、後工程の遅延を引き起こし、半導体装置の製造工程に適さない。ゆえに、40Pa以上で、モル比2.0以下の条件であって実用的な成膜速度膜厚均一性、更には図2に示すように屈折率の大きな変化を生じさせないことを考慮して、適宜、圧力とモル比を選択するとよい。

10 【0020】

【発明の効果】以上説明したように、本発明に係る二酸化珪素の形成方法によれば、減圧条件と成長ガス中のモノシラン濃度とを設定することにより、シリコンクラスタの発生を防止して二酸化珪素膜を形成することができる。そして、減圧条件を少なくとも40Pa以上とし、成長ガス中のモノシランの割合をモノシランと亜酸化窒素との合計量に対してモル比で2.0%以下としたため、膜圧分布の均一性が極めて高い二酸化珪素膜をシリコンクラスタを発生させることなく、実用的な成長速度にて形成することができる。したがって、本発明に係る二酸化珪素の形成方法によれば、形成された二酸化珪素膜でのシリコンクラスタの発生を防止できるため、ひいては、絶縁耐圧等の性能に優れた半導体素子を製造することができるという効果も奏する。

【図面の簡単な説明】

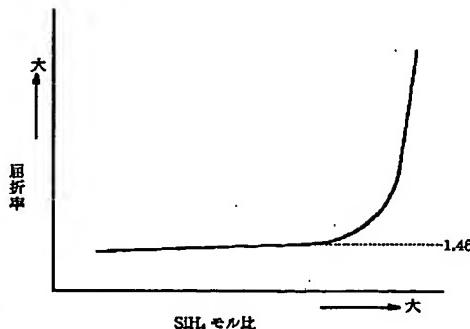
【図1】本発明に係る方法を実施するための装置の一例を示す断面図である。

【図2】モノシラン濃度と二酸化珪素膜の膜質との関係を示すグラフである。

20 30 【符号の説明】

- 1 ヒータ
- 2 外部反応管
- 3 内部反応管
- 4 ポート
- 5 ウエーハ
- 6 ガス導入管
- 7 排気管

【図2】



【図1】

